

Measurement of Actinides in Environmental Samples at Micro-Becquerel Levels by Accelerator Mass Spectrometry

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Title:

**MEASUREMENT OF ACTINIDES IN ENVIRONMENTAL SAMPLES AT
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MEASUREMENT OF ACTINIDES IN ENVIRONMENTAL SAMPLES AT MICRO-BECQUEREL LEVELS BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT

The need for ultra-sensitive actinide measurements continues to expand in the fields of environmental stewardship, nuclear isotope forensics, radiobioassay and environmental research. We have developed a heavy isotope accelerator mass spectrometry (AMS) system at Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry (CAMS). The system was designed particularly for the measurement of actinide concentrations and isotopic ratios. A fast isotope switching capability has been incorporated in the system, allowing flexibility in isotope selection and for the quasi-continuous normalization to a reference isotope spike.

Initially, our utilization of the system has concentrated on the measurement of Pu isotopes. Under current operating conditions, background levels equivalent to $<10^6$ atoms are observed during routine ^{239}Pu and ^{240}Pu measurements. Measurements of samples containing 10^{13} ^{238}U atoms demonstrate that the system provides a ^{238}U rejection factor of $>10^7$. Recently, we have utilized the high dynamic range of the AMS system in measuring samples whose Pu contents ranged from $<10^6$ (background) to $>10^{11}$ Pu atoms. Measurements of known materials, combined with results from an externally organized intercomparison program, indicate that our ^{239}Pu measurements are accurate and precise down to the μBq level ($\sim 10^6$ atoms).

The development of the heavy isotope system was undertaken with particular interest in the measurement of environmental samples, including soils, sediments, waters, air filters, tissue samples, and human urine. The high rejection of interferences, including molecular interferences, and low susceptibility to matrix components, provided by the AMS technique are of particular relevance for such complex samples. These two factors significantly reduce demands on sample preparation chemistry for Pu analyses, allowing relatively simple, cost-effective procedures to be employed. The sensitivity of the AMS technique indicated by our Pu measurements suggests that the further optimization of sample preparation procedures will allow sample size reductions. When such sample preparation improvements are combined with the high sample throughput capabilities of our AMS system, the result will be a rapid and cost-effective measurement technique for actinides in environmental samples.

INTRODUCTION

Accelerator mass spectrometry is an ultra-sensitive technique for the detection of rare isotopes, and the technique is now being routinely applied to a number of long-lived radioisotopes that cannot readily be detected by decay counting. In the application of AMS to the measurement of some of these rare isotopes, 50-100 samples can be measured per day, measurement precisions of

10% or better can be achieved for samples containing $\sim 10^6$ atoms of the rare isotope, and rare-to-stable isotope ratios can be as low as 10^{-14} – 10^{-16} .

In general, samples are prepared as a solid matrix, consisting of an appropriate compound of the element of interest. A metallic carrier, such as silver or iron, is often either integral to the preparation of the sample, or is added to the sample after preparation. For most isotopes being measured by AMS, the final sample that is inserted into the ion source consists of on-the-order of 0.1–10 mg of material, including the metallic carrier, packed into an appropriate target holder.

Negative ions are produced from the sample using a cesium sputter ion source, and these ions are extracted from the ion source and injected into a Tandem Van de Graaff accelerator. The process of acceleration through the accelerator involves the stripping of some electrons from the injected negative ions and produces multiply-charged positively charged ions with energies of 1–100 MeV, depending on the ion of interest and the accelerator being used. The electron stripping process also results in the breakup of negatively charged molecular species that were injected into the accelerator along with the isotopic species of interest; this breakup of molecular species effectively eliminates the possibility of molecular interferences in AMS measurements of actinides. The energetic positively charged ions are then analyzed in the AMS system's high-energy mass spectrometer, and the rare ions are counted individually in a particle detector, typically a gas ionization detector.

In most AMS systems, an associated stable isotope is similarly accelerated and stable isotope ion current measurements are made either simultaneously or quasi-simultaneously with the atom counting measurement of the rare isotope. The result is a measurement of the rare-to-stable isotope ratio, and comparison to similarly measured ratios for standards yields an absolute mass of rare isotope in a sample. In the case of long-lived actinides, isotope spikes are used in place of a naturally occurring stable isotope, analyte-to-spike counts are measured, and comparison to standards yields the absolute mass of the analyte isotope in a sample.

THE CAMS HEAVY-ISOTOPE AMS SYSTEM

Measurement of actinides at CAMS is being undertaken utilizing a recently developed heavy-isotope AMS system that was designed particularly for the measurement of actinide concentrations and isotopic ratios (Figure 1). This heavy-isotope system is comprised of a new heavy-isotope high energy (HE; post-accelerator actinide spectrometer) beamline coupled with a second ion source and modified low-energy (LE; pre-accelerator low energy mass spectrometer) ion transport components. The majority of the funding for the hardware portion of these upgrades and procurements was provided through support from the USDOE Office of Non-Proliferation and National Security (NN-20).

The low energy mass spectrometer section has three main elements: 1) a recently installed high-intensity Cs sputter negative ion source, a spherical electrode ESA, and a 90° bend injection magnet. The current capabilities of, and past developmental work on, the Cs sputter ion sources at CAMS have been described previously [1]. The LE ESA provides sufficient energy resolution to allow high energy sputter tails from the ion source to be rejected before transport to the injection magnet. For actinide measurements the injection magnet is operated to provide

sufficient magnetic rigidity resolution to allow the rejection of $^{238}\text{U}^{16}\text{O}^-$ ions during the injection of $^{239}\text{Pu}^{16}\text{O}^-$ ions.

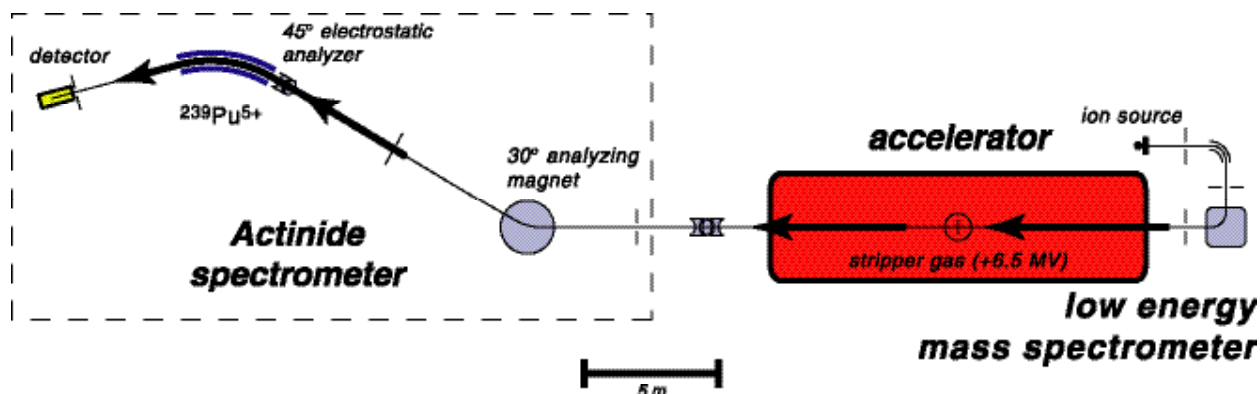


Figure 1. Schematic diagram of the LLNL heavy isotope AMS system.

The heavy-isotope HE beamline was designed to provide transport of ions of mass 200-250 at sufficient energies to allow reasonable transmission, and some level of particle detection and identification. The heavy-isotope HE beamline has two main components: 1) a 30° magnetic bend, and 2) a 45° electrostatic bend. The 30° magnetic bend provides sufficient magnetic rigidity resolution to allow 38 MeV $^{239}\text{Pu}^{5+}$ ions to be cleanly separated from 38 MeV $^{238}\text{U}^{5+}$ ions that may have been injected into the accelerator either as mass peak tails or molecular hydrides of the negative oxide ions being extracted from the ion source for injection. The 45° electrostatic bend is provided by a large Electrostatic Analyzer (ESA) having cylindrical plates with a 5 cm gap, a 4.4 m radius, 45° deflection angle, and 50 kV/cm maximum field (i.e., maximum plate voltages of ± 125 kV). The ESA provides sufficient energy resolution to allow 38 MeV $^{239}\text{Pu}^{5+}$ ions to be cleanly separated from $^{238}\text{U}^{5+}$ having the same magnetic rigidity as the $^{239}\text{Pu}^{5+}$ ions (i.e., $^{238}\text{U}^{5+}$ ions that exited the accelerator with energies slightly higher than 38 MeV because of charge-exchange interactions with residual gases during their acceleration).

RESULTS

Since the commissioning of the heavy isotope AMS system described above in the fall of 2000, we have concentrated our measurement efforts on the Pu isotopes. The measurement programs we have undertaken have centered on the measurement of various types of environmental samples, including soils, sediments, waters, and air filters, and on the measurement of samples pertaining to human exposures to Pu isotopes, e.g., tissue and human urine samples. These programs have included measurements as a part of the USDOE Marshall Islands Program and internally funded LLNL research programs. In the past year of operations we have been able to undertake the optimization of the operating conditions of the heavy isotope AMS system and have demonstrated routine measurement capabilities for Pu isotopes.

As a part of our efforts in the development of routine operating conditions and to monitor the performance of our system, we routinely prepare and measure replicate samples derived from a calibrated ^{239}Pu solution (IPL 630-22-3) which span the isotope concentration range of interest

for particular studies. Typical results obtained from such a series of replicates are shown in Figures 2 and 3.

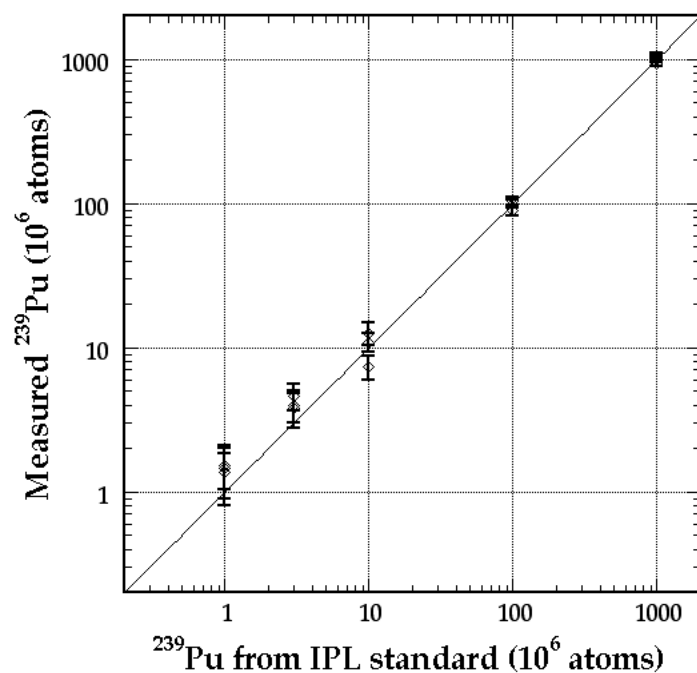


Figure 2. Measurements of samples derived from a calibrated ^{239}Pu solution (IPL 630-22-3) spanning the range from 10^6 atoms to 10^9 atoms.

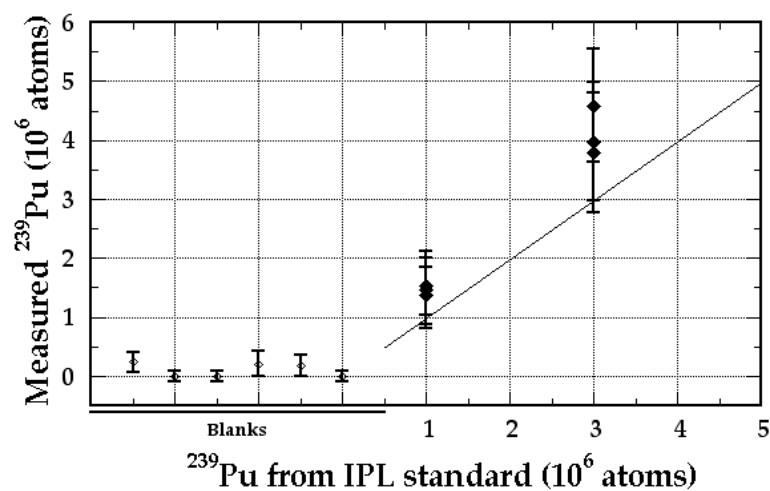


Figure 3. Measurements of samples derived from a calibrated ^{239}Pu solution (IPL 630-22-3). (lower range of Figure 2 with blank sample results - blank levels are equivalent to $< 0.5 \mu\text{Bq}$).

Results obtained from such measurements undertaken during a variety of studies demonstrate that the heavy isotope AMS system as it is currently operated has a linear measurement dynamic range of greater than 5 orders of magnitude. Measurements of prepared “Pu blank” samples demonstrate that background levels equivalent to $<10^6$ atoms are observed during routine ^{239}Pu and ^{240}Pu measurements. Blank sample results have shown ongoing improvements over the last year with more recent ^{239}Pu and ^{240}Pu measurement background levels falling below 5×10^5 atoms (Figure 3).

We also routinely monitor the effectiveness of the heavy isotope AMS system in rejecting ^{238}U interferences through measurements of “Pu blank” samples that have been spiked with 10^{13} – 10^{14} atoms of depleted ^{238}U . The results of these measurements demonstrate that the heavy isotope AMS system provides a ^{238}U interference rejection factor of $>10^7$ during routine ^{239}Pu measurements. This high rejection of ^{238}U interferences implies that environmental samples can be prepared for Pu measurements using relatively routine and simple chemical procedures which contributes significantly to the development of the heavy isotope AMS system as a rapid and cost-effective measurement technique for Pu in environmental samples.

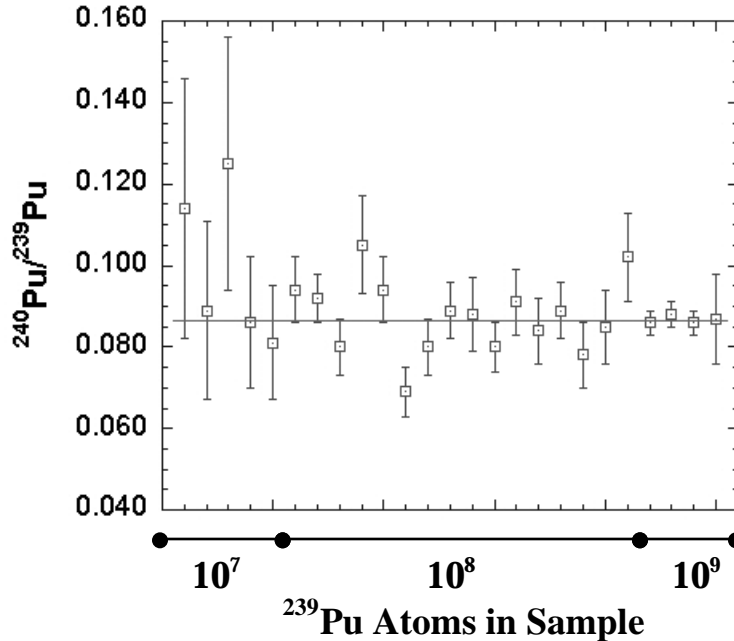


Figure 4. Measurements of samples prepared from CRM 138 (horizontal line: $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of CRM 138 calculated from certified atom percent contents of CRM 138).

In addition to the above measurements, we routinely measure samples prepared from traceable Pu isotopic standards (CRM 128 and CRM 138) to test the overall instrument performance. As a part of these measurements we have looked for mass-dependent normalization factors for our ^{239}Pu , ^{240}Pu and ^{242}Pu isotope measurements. Under our routine operating conditions we have found that the measured ratios are accurate within their uncertainties and do not show significant evidence of mass-dependent biases. For example, the weighted mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of the results shown in Figure 4 of 0.086 ± 0.06 ($n=25$) agrees within uncertainty estimates with the

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.0863 ± 0.0001 calculated from the certified atom percent contents of CRM 138.

In order to have an independent evaluation of the performance of the heavy isotope AMS system in measurements of “real world” samples, we participated in the “Second Laboratory Intercomparison Study for the Determination of μBq Quantities of ^{239}Pu in Synthetic Urine by Mass Spectrometric and Fission Track Analyses” [2,3]. The study was supported by the DOE Office of International Health with the participation of several laboratories measuring Pu by various techniques, with LLNL being the only AMS system in the study.

The NIST prepared synthetic urine samples contained ^{239}Pu , natural uranium and ^{240}Pu . The amount of uranium added was 0.05 Bq per sample, which is approximately the background level observed in human urine samples from the vicinity of Los Alamos, NM. Plutonium-240 was added at the global fallout ratio $^{240}\text{Pu}/^{239}\text{Pu} \sim 0.15$. Five testing levels of ^{239}Pu were prepared: 0 (blank), 20, 50, 150, and 280 $\mu\text{Bq/L}$; five samples per nonzero level and eight blanks were submitted randomly and blindly to each of the participating laboratories.

The AMS results obtained for the NIST prepared synthetic urine samples are shown in Figures 5 and 6.

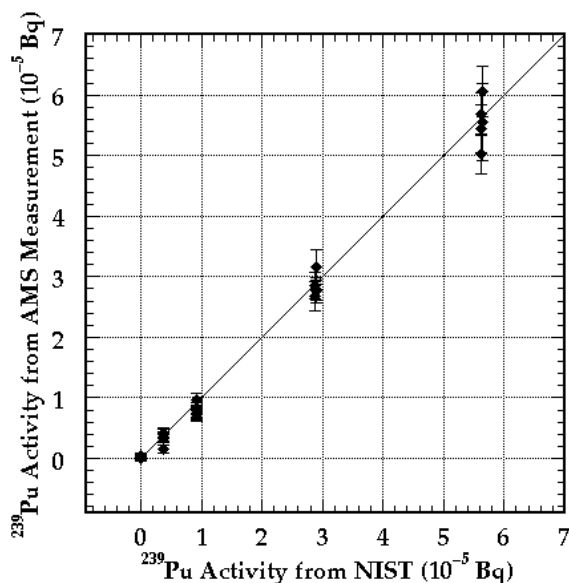


Figure 5. ^{239}Pu activities of NIST supplied synthetic urine samples compared to ^{239}Pu activities derived from AMS measurements of ^{239}Pu contents of samples.

For our AMS measurements, the samples were prepared following the standard protocol used for Pu alpha spectrometry by the LLNL Marshall Islands Program with a few modifications to obtain a suitable target for AMS measurement. Plutonium-242 was added as a recovery tracer, which is common practice in alpha spectrometry, and is also required for the AMS determination of Pu isotopes; for these samples we used our routine 3.0×10^9 atoms of ^{242}Pu for the AMS

spike. After acid digestion and ion exchange separation, Pu(IV) was coprecipitated with ~0.3 mg of Fe(III) and Nb(V) by adding ammonia. The precipitate was centrifuged, washed, calcined at 800°C in a quartz crucible, and loaded in an aluminum target holder. The target holders were then placed in the 64-sample wheel of the ion source, and the $^{239}\text{Pu}/^{242}\text{Pu}$ and $^{240}\text{Pu}/^{242}\text{Pu}$ ratios in the synthetic urine samples were determined using the heavy isotope AMS system. The known amount of ^{242}Pu spike added was then used to calculate the numbers of ^{239}Pu and ^{240}Pu atoms in the samples. Subsequently, the total and per unit mass activities in the sample, along with corresponding standard deviations, were calculated and submitted to the exercise evaluators.

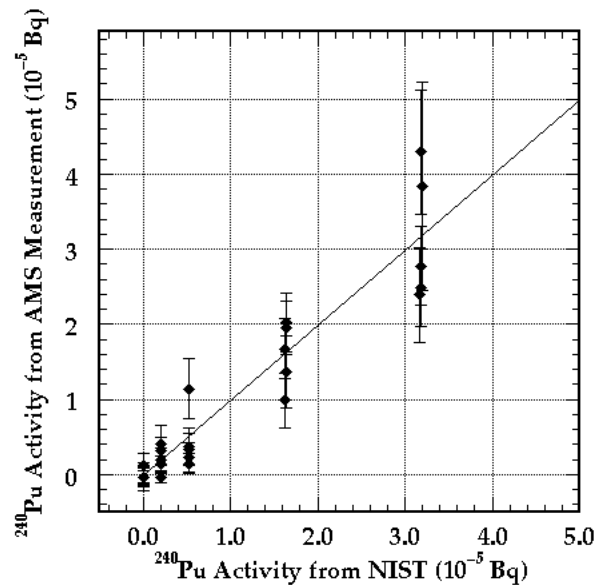


Figure 6. ^{240}Pu activities of NIST supplied synthetic urine samples compared to ^{240}Pu activities derived from AMS measurements of ^{240}Pu contents of samples.

Statistical analysis of these results by the study evaluators [2] provided a number of significant results: 1) Precision of AMS results – The precision of the analysis was evaluated for each test level using two methods. The first method used the coefficient of variation for each test level while the second method, taken from ANSI N13.30, relied on the standard deviation of the bias and can not be used for blanks. For the AMS results, the precisions obtained by both methods were similar with average values of 6.3, 6.5, 11, and 30% for ^{239}Pu activities of 55, 28, 8.9, and 3.6 μBq , respectively. In the determination of ^{240}Pu the precision averages are 26, 26, 80, and 81%, for activities of 31, 16, 5.1, and 2.0 μBq , respectively, 2) ANSI N13.30 precision and bias criteria – The AMS measurements met the ANSI N13.30 precision and bias criteria for both ^{239}Pu and ^{240}Pu at all test levels, and 3) The minimum detectable amount (MDA) was determined by two methods, one based on the work of Currie and the other on a regression method, resulting in MDA values of 0.82 and 6.1 μBq for ^{239}Pu , and 2.1 and 14 μBq for ^{240}Pu , respectively.

One significant implication of these results is that ^{238}U interferences would appear to have had no impact on the precision and accuracy of the AMS measurements. This demonstrates that the high ^{238}U rejection provided by the heavy isotope AMS system can be combined with routine, relatively simple sample preparation chemistry to produce measurements of ^{239}Pu and ^{240}Pu at μBq levels in samples containing significant amounts of ^{238}U .

SUMMARY

We have developed a heavy isotope AMS system at Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry. The system incorporates a number of features to allow the rapid and cost-effective measurement of actinide concentrations and isotopic ratios. In particular, the beamline and data acquisition systems were designed to include a fast isotope switching capability that allows quasi-continuous normalization to a reference isotope spike and considerable flexibility in isotope selection.

With the establishment of routine operating conditions for the measurement of Pu isotopes, we have been able to quantify various capabilities of the heavy isotope AMS system. Current observed background levels are equivalent to $<10^6$ atoms during routine ^{239}Pu and ^{240}Pu measurements. Measurements at ^{239}Pu settings of samples containing 10^{13} ^{238}U atoms demonstrate that the heavy isotope AMS system provides a ^{238}U rejection factor of $>10^7$. Measurements of samples derived from a calibrated ^{239}Pu solution demonstrate that the measurement system has a linear dynamic Pu measurement range from $<10^6$ atoms to $>10^{11}$ atoms. Results from the NIST organized 2nd Laboratory Intercomparison Study demonstrate that our ^{239}Pu measurements of ^{239}Pu and ^{240}Pu contents of "real world" samples are accurate and precise down to the μBq level ($\sim 10^6$ ^{239}Pu atoms).

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